

RELATED APPLICATIONS

This application is a continuation of my co-pending U.S. patent application Serial No. 09/739,536 filed December 15, 2000 for "Determination of Multi-Valent Metal Contamination and System for Removal of Multi-Valent Metal Contaminants from Water."

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advantage of this method is the reduction in the amount of resultant sludge, this system must be operated continuously so as to be most effective in achieving a predetermined set point of heavy metal concentration in solution. Moreover, it is not very effective and still leaves substantial amounts of trace heavy metals in the water.

U.S. Patent No. 5,000,858 to Manning and Wells sets forth a method for removing hexavalent chromium from water which employs two or more reactors for treating waste water. Each reactor contains a flocculator and a clarifier for batch treatment in an acidic medium below a pH of 3. A reducing agent is added and the pH is thereafter increased to an alkaline pH where the water is then transferred to the second reactor having a flocculator. In this case, a flocculent is added and the solution is then transported to a clarifier where the heavy metal-containing solids are removed.

U.S. Patent No. 5,000,859 to Suciu, et al discloses a process in which a sodium sulfide/ferrous sulfate treatment is used to remove hexavalent chromium, as well as other potentially toxic metals, from industrial waste waters. This patent discloses the use of sulfur dioxide, sodium sulfite, sodium bisulfite, sodium borohydride, and the use of ferrous ions as reducing agents. This

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method relies upon reduction of Cr^{+6} to Cr^{+3} in a pH range of about 7 to 9 by addition of ferrous ions from ferrous sulfate followed by sulfide or more ferrous ions to induce precipitation of the Cr^{+3} and of other reduced heavy metals. Polymers are added to aid.

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In the above reactions (2) and (3), the ferrous ions represent the reduced (Fe II) form of iron, as ferrous sulfate heptahydrate, $\text{Fe}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ having a formula weight of 278.01 daltons, or otherwise, a cobaltous compound (Co II) acetate tetrahydrate, $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, with a formula weight of 249.08 daltons. The source of the oxidized chromium, the contaminant, is frequently sodium chromate as in the example above, $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ with a formula weight of 234.06 daltons. The reduced chromium (Cr^{+3}) often exists as chromium trichloride (CrCl_3) with a formula weight of 158.38 daltons.

When the reductant is added to water, it can be added in a relatively small amount as, for example, one ounce of ferrous sulfate to about one hundred milliliters of water. This yields a solution concentration of 1.02 molar Fe II. There is no specific required amount for the addition of the reducing agent, except that the reducing agent should be present in an amount of sufficient concentration to reduce essentially all of the reducible metal contaminant in the water. A simple series of dilutions can be used with an aliquot of the water to be tested to determine the desired range of concentration of the reductant. Alternatively, an aliquot of treated water can be pre-tested with additional reductant to see if any further change in color occurs.

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A variety of reducing agents can be used in this determination and, incidentally, the same reducing agents would be used in the process, as hereinafter described. These reducing agents are usually maintained at an acidic pH between 2.5 to about 6.5 in

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metallic reductants, the available valence states are given and, particularly, the unoxidized state, the chemical formula and the color in the reduced state, if applicable.

1. Cerium, Ce (valence states: III, IV), 140.12, Rare Earth Group.

- (a) Ce(III) acetate, $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3$, 317.26, colorless.
- (b) Ce(III) acetate hydrate, $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, 344.28, white-reddish.
- (c) Ce(III) sulfate, $\text{Ce}_2(\text{SO}_4)_3$, 568.42, colorless to green.
- (d) Ce(III) sulfate/pentahydrate, $\text{Ce}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ 658.50.
- (e) Ce(III) sulfate octahydrate, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, 712.54, pink.
- (f) Ce(III) sulfate nonahydrate, $\text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, 730.56.

2. Cobalt, Co (II, III), 58.933, Iron-Cobalt Group.

- (a) Co(II) acetate tetrahydrate, $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, 249.08, red-violet.
- (b) Co(II) bromide, CoBr_2 , 218.75 green.
- (c) Co(II) bromide hexahydrate, $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$, 326.84, red-violet.
- (d) Co(II) chloride, CoCl_2 , 129.84, blue.
- (e) Co(II) chloride dihydrate, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, 165.87, red-violet.
- (f) Co(II) chloride hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 237.93, red.

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- (g) Co(II) iodide (α), CoI_2 , 312.74, black.
- (h) Co(II) iodide (β), CoI_2 , 312.74, yellow.
- (i) Co(II) iodide dihydrate, $\text{CoI}_2 \cdot 2\text{H}_2\text{O}$, 348.77, green.

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- (j) Co (II) iodide hexahydrate, $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$, 420.83, brown-red.
 - (k) Co(II) nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 291.04, red.
 - (l) Co(II) sulfate, $\text{Co}(\text{SO}_4)$, 155.00, dark bluish.
 - (m) Co(II) sulfate monohydrate, $\text{Co}(\text{SO}_4) \cdot \text{H}_2\text{O}$, 173.01, red.
 - (n) Co(II) sulfate hexahydrate, $\text{Co}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$, 263.09, red.
 - (o) Co(II) sulfate heptahydrate, $\text{Co}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$, 281.10, red-pink.
3. Europium, Eu (II, III), 151.96, Rare Earth Group.
- (a) Eu(II) bromide, EuBr_2 , 311.78.
 - (b) Eu(II) chloride, EuCl_2 , 222.87, white.
 - (c) Eu(II) iodide, EuI_2 , 405.77, brown-olive green.
4. Iron, Fe (II, III), 55.847, Iron-Cobalt Group.
- (a) Fe(II) acetate tetrahydrate, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, 246.00 light green.
 - (b) Fe (II) bromide, FeBr_2 , 215.67, green-yellow.
 - (c) Fe (II) chloride, FeCl_2 , 126.75, green to yellow.
 - (d) Fe(II) chloride dihydrate, $\text{FeCl}_2 \cdot \text{H}_2\text{O}$, 162.78. green.
 - (e) Fe(II) chloride tetrahydrate, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 198.81, blue-green.
 - (f) Fe(II) iodide, FeI_2 , 309.66, gray.

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- (g) Fe(II) iodide tetrahydrate, $\text{FeI}_2 \cdot \text{H}_2\text{O}$ 381.72.
- (h) Fe(II) nitrate hexahydrate, $\text{Fe}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 287.95, green.
- (i) Fe(II) sulfate tetrahydrate, $\text{Fe}(\text{SO}_4) \cdot 4\text{H}_2\text{O}$, 224.01, green.
- (j) Fe(II) sulfate pentahydrate, $\text{Fe}(\text{SO}_4) \cdot \text{H}_2\text{O}$, 242.02, white.

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- (k) Fe(II) sulfate heptahydrate, $\text{Fe}(\text{SO}_4) \cdot \text{H}_2\text{O}$, 278.05, blue-green.

5. Manganese, Mn (II, III), 54.938, Transition (VII b) Group.

- (a) Mn(II) acetate tetrahydrate, $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, 245.08, pale red.
- (b) Mn(II) bromide, MnBr_2 , 214.76, rose.
- (c) Mn(II) bromide tetrahydrate, $\text{MnBr}_2 \cdot \text{H}_2\text{O}$, 286.82, rose.
- (d) Mn(II) chloride, MnCl_2 , 125.84, pink.
- (e) Mn(II) chloride tetrahydrate, $\text{MnCl}_2 \cdot \text{H}_2\text{O}$, 197.91, rose.
- (f) Mn(II) iodide, MnI_2 , 308.75, rose.
- (g) Mn(II) iodide tetrahydrate, $\text{MnI}_2 \cdot \text{H}_2\text{O}$, 380.81, rose.
- (h) Mn(II) sulfate, $\text{Mn}(\text{SO}_4)$, 151.00, reddish.
- (i) Mn(II) sulfate monohydrate, $\text{Mn}(\text{SO}_4) \cdot \text{H}_2\text{O}$, 169.01, pale pink.
- (j) Mn(II) sulfate tetrahydrate, $\text{Mn}(\text{SO}_4) \cdot \text{H}_2\text{O}$, 223.06, pink.
- (k) Mn(II) sulfate pentahydrate, $\text{Mn}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, 241.08, rose.
- (l) Mn(II) sulfate heptahydrate, $\text{Mn}(\text{SO}_4) \cdot \text{H}_2\text{O}$, 277.11, red.

6. Nickel, Ni (II, III), 58.71, Transition (VIII) Group.

- (a) Ni(II) acetate, $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2$, 176.80, green.
- (b) Ni(II) acetate tetrahydrate, $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, 248.86,

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green.

(c) Ni(II) bromide, NiBr_2 , 218.53, yellow brown.

(d) Ni(II) bromide trihydrate, $\text{NiBr}_2 \cdot \text{H}_2\text{O}$, 272.57, yellowish green.

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- (e) Ni(II) chloride, NiCl_2 , 129.62, yellow.
 - (f) Ni(II) chloride hexahydrate, $\text{NiCl}_2 \cdot \text{H}_2\text{O}$, 237.70, green.
 - (g) Ni(II) iodide, NiI_2 , 312.52, black.
 - (h) Ni(II) nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 290.81, green.
 - (i) Ni(II) sulfate, $\text{Ni}(\text{SO}_4)$, 154.78, yellow.
 - (j) Ni(II) sulfate hexahydrate, $\text{Ni}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$, 262.86, green to blue.
 - (k) Ni(II) sulfate heptahydrate, $\text{Ni}(\text{SO}_4) \cdot \text{H}_2\text{O}$, 280.88, green.
7. Platinum, Pt (II, III, IV), 195.09, Platinum Group.
- (a) Pt(II) chloride, PtCl_2 , 266.00, olive green.
 - (b) Pt(III) chloride, PtCl_3 , 301.45, greenish black.
8. Praseodymium, Pr (III, IV), 140.907 Rare Earth Group.
- (a) Pr(III) acetate trihydrate, $\text{Pr}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$, 372.09, green.
 - (b) Pr(III) chloride, PrCl_3 , 247.27, blue green.
 - (c) Pr(III) chloride heptahydrate, $\text{PrCl}_3 \cdot \text{H}_2\text{O}$, 373.37, green.
 - (d) Pr(III) iodide, PrI_3 , 521.62, green.
 - (e) Pr(III) sulfate, $\text{Pr}_2(\text{SO}_4)_3$, 570.00, light green.
 - (f) Pr(III) sulfate pentahydrate, $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ 660.08.
 - (g) Pr(III) sulfate octahydrate, $\text{Pr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, 714.12, green.

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9. Rhenium, Re (III, IV, V), 186.2, Transition (VII b) Group.
- (a) Re(III) chloride, ReCl_3 , 292.56, dark red.
 - (b) Re(IV) chloride, ReCl_4 , 328.01, black.

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10. Rhodium, Rh (II, III, IV), 102.905, Platinum Group.
- (a) Rh(III) chloride hydrate, $\text{RhCl}_3 \cdot \text{H}_2\text{O}$, dark red.
 - (b) Rh(II) nitrate dihydrate, $\text{Rh}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, 262.905, red.
 - (c) Rh(III) sulfate tetrahydrate, $\text{Rh}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, 566.05, red.
 - (d) Rh(III) sulfate dodecahydrate, $\text{Rh}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, 710.18, pale yellow.
 - (e) Rh(III) sulfate pentadecahydrate, $\text{Rh}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, 764.22, light yellow.
11. Samarium, Sm (II, III), 150.35, Rare Earth Group.
- (a) Sm(II) chloride, SmCl_2 , 221.26, red-brown.
12. Terbium Tb (III, IV), 158.924, Rare Earth Group.
- (a) Tb(III) bromide, TbBr_3 , 398.65.
 - (b) Tb(III) chloride hexahydrate, $\text{TbCl}_3 \cdot \text{H}_2\text{O}$, 373.78, colorless.
 - (c) Tb(III) fluoride, TbF_3 , 215.92.
 - (d) Tb(III) iodide, TbI_3 , 539.64.
 - (e) Tb(III) nitrate hexahydrate, $\text{Tb}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, 453.03, colorless.
 - (f) Tb(III) sulfate octahydrate, $\text{Tb}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, 750.16, white.

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13. Tin, Sn (II, IV), 118.69, IV a Group Metals.
- (a) Sn(II) bromide, SnBr_2 , 278.51, pale yellow.
 - (b) Sn(II) chloride, SnCl_2 , 189.60, white.
 - (c) Sn(II) fluoride, SnF_2 , 156.69, white.

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and that the metal contaminant had been reduced. Generally, although not in all cases, the reductant forms of hydroxides are co-precipitated with the hydroxides of the reduced contaminant metal. The remaining (non-precipitated) oxidized metal reductant would be replenished and/or re-converted by reduction from its higher valence state to its lower or reduced valence state. For iron salts, color changes from yellow-green to amber, depending on concentrations of specific iron salt ions are also associated with conversion of Fe^{+2} to Fe^{+3} .

The complexing agent would normally be a dicarboxylic acid or a tricarboxylic acid. These particular acids act as chelating or sequestering agents and thereby stabilize the reductant, but do not interfere with their reducing properties. Some of the suitable sequestering agents which may be used include, for example, fumaric (trans-1,2-ethylenedicarboxylic) acid, malic (hydroxysuccinic) acid, and succinic (ethanedicarboxylic) acid. Some of the tricarboxylic acids which may be used include aconitic acid (1-propene-1,2,3-tricarboxylic acid) and citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid).

Maintaining an acid pH roughly between 1.0 to 6.5 and, preferably, between 2.5 to 4.5, in the reactor is desirable because the carboxyl groups of these dicarboxylic and tricarboxylic acids

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would be protonated relative to their pK values. In this way, the metal ion of the reducing agent could enter into an exchange reaction with the protons of the carboxylic acid groups which would provide stabilization of the reducing agents.

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